

Short Communication

Fabrication and charge/discharge behaviour of some lithium solid polymer electrolyte cells [☆]

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Abstract

A report is given of the fabrication of some laboratory model lithium cells using solid polymer electrolytes (SPE). These SPEs are based on poly(ethylene oxide) (PEO) and lithium picrate/lithium lactate salts. Electrochemical parameters (i.e., open-circuit potential, short-circuit current) and the discharge behaviour under different current drains of these cells are studied. The behaviour of cells with SPE blended with plasticizer like polyethylene glycol is also examined. It has been observed that a lithium cell with a PEO/lithium picrate electrolyte in combination with a picrate-doped polypyrrole cathode behaves excellently compared with other systems. The results are explained in terms of higher ion conductivity of PEO/picrate salt complexes.

Keywords: Solid polymer electrolytes; Lithium lactate; Lithium picrate

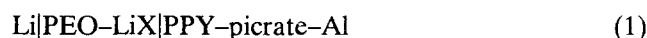
1. Introduction

Electrochemical cells using solid polymer electrolytes (SPEs) have several advantages over conventional cells with liquid systems. Among these are a low self-discharge rate, extreme chemical stability, a leak-proof nature, and small dimensions.

Armand and co-workers [1,2] first applied a solid polymer electrolyte of poly(ethylene oxide) (PEO) and lithium salt complex some fifteen years ago. Since then, several laboratories [3–6] have undertaken research and development programmes on SPE batteries. Most of these studies are confined to a PEO-based solid polymer electrolyte with lithium salts of ClO_4^- or CF_3SO_3^- . Recently, the authors have reported [7] studies on solid polymer electrolytes using PEO and lithium salts of certain organic acids. To date, however, a polymer matrix consisting of salts of organic acids [8,9] has not been applied in lithium battery systems.

Thus, the intention of the present study is to fabricate lithium cells using SPEs of PEO/lithium picrate and PEO/lithium lactate in combination with a conducting

polymer-coated cathode. The battery configuration so formed, may be represented as:



where X = picrate, lactate, and PPY = polypyrrole.

2. Experimental

2.1. Materials

Poly(ethylene oxide) (BDH, USA) with an approximate mol. wt. of 6×10^5 , lithium lactate (BDH, UK), and LiClO_4 (Aldrich) were used as all materials. Lithium picrate was prepared by the procedure reported previously [10]. Lithium metal (Merck, Germany) was used as a thin metal sheet. Pyrrole (Merck, Germany) was used as received, while picric acid (Glaxo, UK) was employed without further purification. Acetonitrile (BDH) was purified by successive distillation from P_2O_5 and CaH_2 , after initial drying with CaH_2 [11]. Methanol (Bengal Chemical and Pharmaceuticals) was dried over activated magnesium turnings [12] and fractionally distilled. Polypyrrole was deposited on aluminium foil of high purity (Johnson-Matthey) and this served as the cathode material in the fabricated all polymer lithium

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cells. Poly(ethylene glycol) (PEG) 6000 (supplied by Lubrizol India Ltd., on request) was used as received.

2.2. Preparation

2.2.1. Electrolyte

The SPEs were prepared by the usual method of solution casting from acetonitrile or methanol. The details of SPE preparation have been described earlier [7].

2.2.2. Cathode

Polypyrrole-coated aluminium foils doped with picrate ions were used as the cathode material in the constructed lithium cells. Picrate-doped polypyrrole deposition on aluminium of high purity and size 2 cm × 2 cm was slightly different from that reported for iron [13]. An extended part of aluminium-sheet acted as a current connector.

2.2.3. Anode

A sheet of lithium metal with a size slightly greater than 2 cm × 2 cm was used. It was degreased with dry-distilled acetone and then the oxide coating was removed with a sharp nickel knife. The resulting, silver coloured, lithium metal was employed as an anode in the all solid lithium cells. The sheet-metal anode was joined to a nickel current-connector.

2.3. Fabrication of all solid polymer lithium cell

Small-scale, sandwich-type, lithium cells of 4 cm² size were constructed. A schematic of the cells is given in Fig. 1. Thin films of SPEs were cut into squares of size 2 cm × 2 cm by a sharp blade. The electrolyte was

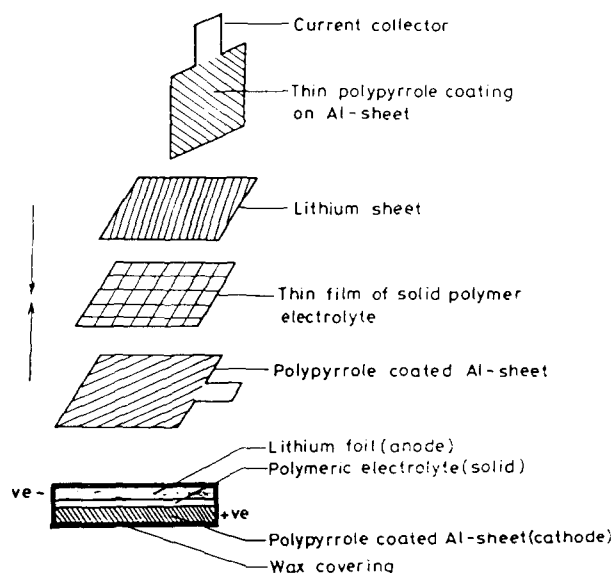


Fig. 1. Schematic of thin-film battery in cross section and general view.

sandwiched between the lithium-sheet anode and the aluminium-polypyrrole-picrate cathode after moistening the electrolyte with the selected solvent. The cathode and anode were pressed to improve the contact and the compactness of the cell. After this, the cell was dipped into hot wax that covered the cell after hardening at room temperature. The cells were maintained at an ambient temperature of 27 °C for 1 h and then electrochemical studies were performed.

3. Results and discussion

The room-temperature performance of the fabricated lithium cells with SPE electrolytes was determined in terms of the open-circuit potential (OCP) and the short-circuit current (SCC) by means of a MIC-6000E multimeter (made in Taiwan). Discharge studies were undertaken at different current drains. The discharge curves of the cells are given in Figs. 2 and 3.

The OCP and SCC of the laboratory-scale all solid lithium cells are listed in Tables 1 and 2. The OCP values of cells containing SPEs with different concentrations of the same lithium salt are almost same but the SCC values vary with concentration. In all cases, the highest SCC value is observed for a 5:1 PEO-lithium salt ratio. This may be due to the fact that the con-

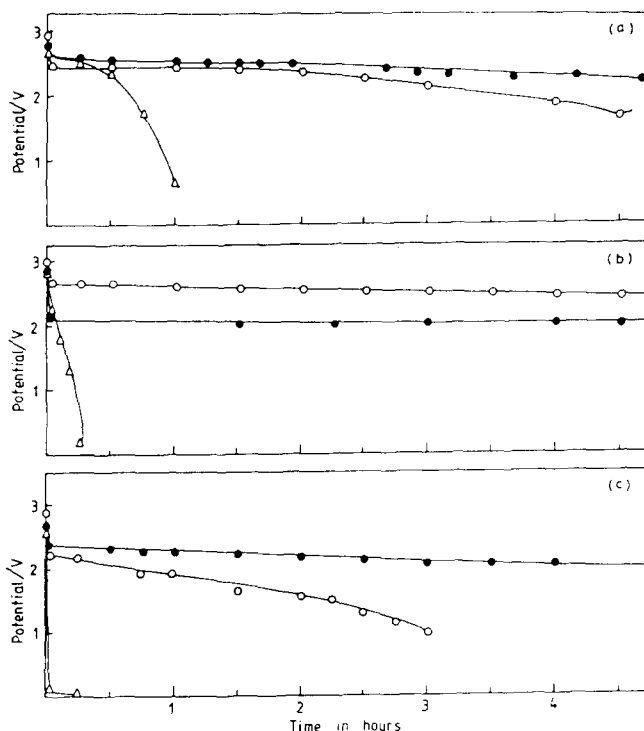


Fig. 2. Discharge study of the cells; (a) Li|PEO-LiX(20:1)|PPY-lithium picrate-Al; (b) Li|PEO-LiX(10:1)|PPY-lithium picrate-Al, and (c) Li|PEO-LiX(5:1)|PPY-lithium picrate-Al at 2 μ A continuous current drain. (—○—) PEO-lithium picrate; (—△—) PEO-lithium lactate, and (—●—) PEO-LiClO₄ electrolyte.

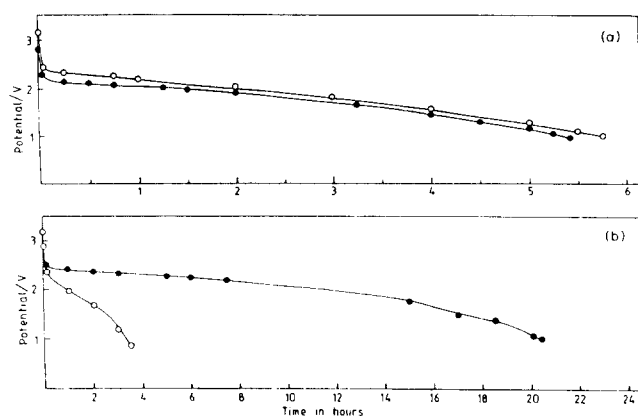


Fig. 3. Discharge study of cells: (a) Li|(0.75 PEO + 0.25 PEG)-LiX(20:1)|PPY-lithium picrate-Al; (b) Li|(0.5 PEO + 0.5 PEG)-LiX(20:1)|PPY-lithium picrate-Al at 5 μ A current drain. (—○—) (PEO + PEG)-lithium picrate, and (—●—) (PEO + PEG)-LiClO₄ electrolyte.

Table 1
Electrochemical parameters of SPEs and fabricated SPE lithium cell having configuration Li|(PEO)-LiX|PPY-Al

Solid polymer electrolyte	Ratio (wt./wt.)	OCP (V)	SCC (μ A)
PEO-lithium picrate	20:1	2.96	12.5
	10:1	2.96	17.8
	5:1	2.95	35.2
PEO-lithium lactate	20:1	2.76	7.2
	10:1	2.76	9.2
	5:1	2.72	10.3
PEO-LiClO ₄	20:1	2.79	39.9
	10:1	2.77	45.2
	5:1	2.75	72.2

Table 2
Electrochemical parameters of fabricated lithium cells with a composite polymer electrolyte of configuration:

Li|(xPEO + yPEG)-LiX|PPY-Al *

Composition of the composite polymer electrolyte	Ratio (wt./wt.)	OCP (V)	SCC (μ A)
PEO-lithium picrate	20:1	2.96	35.2
(0.75PEO + 0.25PEG)-lithium picrate	20:1	3.18	77.0
(0.5PEO + 0.5PEG)-lithium picrate	20:1	3.18	118.0
PEO-lithium lactate	20:1	2.76	8.6
(0.75PEO + 0.25PEG)-lithium lactate	20:1	2.82	12.2
(0.5PEO + 0.5PEG)-lithium lactate	20:1	2.80	15.3
PEO-LiClO ₄	20:1	2.79	76.8
(0.75PEO + 0.25PEG)-LiClO ₄	20:1	2.78	368.0
(0.5PEO + 0.5PEG)-LiClO ₄	20:1	2.79	485.0

* X = lithium picrate or lithium lactate.

ductivity is highest at this concentration, as expected from the amorphous nature of these salts. The OCP value of the cells containing lithium picrate-based SPEs are higher due to the reversibility of the picrate ion with respect to SPE and the picrate-doped polypyrrole cathode.

All the cells were discharged at a continuous current drain of 2 μ A at 27 °C. The discharge behaviour of the cells containing a lithium lactate-based SPE is not at all satisfactory. This is probably due to a slow charge transfer (ion diffusion) through the PEO-lithium lactate complex because of its relatively high crystallinity, and also because of the non-reversibility of the doping ion. The discharge behaviour of the cells with a PEO/lithium picrate complex in a 10:1 concentration exhibits better performance. At other concentrations, the picrate ion containing SPE behaves similar to perchlorate, while the performance of lithium lactate is inferior.

The electrochemical parameters and the discharge behaviour of a large number of cells reported in the literature [5,14,15] are almost similar to the present cells. In the presence of a poly(ethylene glycol) plasticizer, the polymer electrolyte so formed enhances the electrochemical parameters of the cells (see Table 2). The OCP values of the cells based on a lithium picrate composite polymer electrolyte are markedly increased. Cells with a composite polymer electrolyte were discharged at a continuous current drain of 5 μ A. A cell with a composition 75% PEO, 25% PEG and lithium picrate displays better performance. At this particular composition, the SPE exhibits a strong amorphous nature.

4. Conclusions

Investigations on laboratory-scale, solid polymer electrolyte lithium cells indicate that, apart from the PEO-lithium lactate cell, the systems have promising features for low-drain use. The behaviour of PEO/lithium picrate cells is almost parallel to that of well-studied lithium cells with a PEO-LiClO₄-based electrolyte. Considering the easy fabrication of the picrate-reversible, light (Al) polymer cathode, however, the PEO/lithium picrate SPE may show promise as a practical rechargeable polymer battery.

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